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(54) COMBUSTION SYSTEM

(57) A combustion system operated at low cost is provided. A combustion system 1 includes a combustion device 10 that burns fuel, an exhaust line L1 through which exhaust gas flows, the exhaust gas being generated through combustion of the fuel in the combustion device 10, an air preheater 30 that is disposed in the exhaust line L1 and that recovers heat from the exhaust gas, and a denitration device 40 that is disposed in the exhaust line L1 and that removes nitrogen oxide from the exhaust gas using a denitration catalyst. The denitration device 40 is disposed downstream from the air preheater 30 in the exhaust line L1, and the denitration catalyst contains 43 wt% or more of vanadium pentoxide and has a BET specific surface area of 30 m^2/g or more.

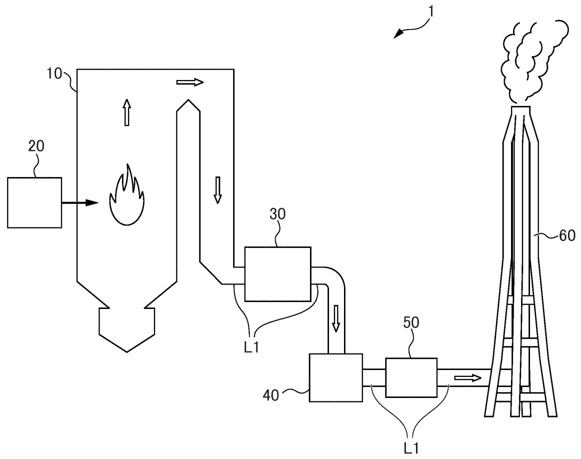

FIG. 1

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Description

TECHNICAL FIELD

[0001] The present invention relates to a combustion system. More specifically, the present invention relates to a combustion system including a combustion device, an exhaust line through which exhaust gas flows, an air preheater that recovers heat from the exhaust gas, and a denitration device that removes nitrogen oxide from the exhaust gas.

BACKGROUND ART

[0002] In existing combustion systems including a boiler, thermal energy is generated as a result of combustion of fuel such as coal in the boiler, and then, for example, the thermal energy is converted into electric energy. The combustion of fuel in the boiler generates an exhaust gas containing nitrogen oxide.

[0003] The exhaust gas generated in the boiler is discharged to the outside from the boiler through an exhaust line. In consideration of environmental factors, nitrogen oxide is removed, by a denitration device, from the exhaust gas that is discharged to the outside from the boiler.

[0004] In general, a denitration catalyst such as a vanadium/titanium catalyst (V_2O_5/TiO_2) is used for denitration devices that remove nitrogen oxide from exhaust gas. The vanadium/titanium catalyst exhibits high catalytic activity in a high-temperature (e.g., about 370°C) environment. Therefore, such a denitration device is disposed in an area near the outlet of exhaust gas in a boiler or on the upstream side of an exhaust line in, for example, a thermal power plant (e.g., refer to Patent Document 1).

[0005] Patent Document 1: Japanese Unexamined Patent Application, Publication No. 2011-190940

DISCLOSURE OF THE INVENTION

Problems to be Solved by the Invention

[0006] However, such an area near the outlet of exhaust gas in a boiler or on the upstream side of an exhaust line is in a high-temperature environment as described above and furthermore coal ash and S components are present in a high concentration, which readily deteriorates the denitration catalyst. If the denitration catalyst rapidly deteriorates, the denitration catalyst needs to be frequently replaced and thus the operation cost of the combustion system tends to increase.

[0007] In the case where nitrogen oxide is removed from exhaust gas by a selective catalytic reduction method in the denitration device, if the denitration catalyst deteriorates, ammonia used as a reducing agent leaks from the denitration device. If ammonia leaks from the denitration device, the ammonia and S components in the exhaust gas react with each other to generate ammonium sulfate. The ammonium sulfate adheres to an air preheater disposed downstream from the denitration device. When ammonium sulfate adheres to and deposits on the air preheater, for example, the air preheater needs to be cleaned to prevent clogging of a flow path of exhaust gas, which further increases the operation cost of the combustion system.

[0008] In view of the foregoing, it is an object of the present invention to provide a combustion system operated at low cost. Means for Solving the Problems

[0009] The present invention relates to a combustion system including a combustion device that burns fuel, an exhaust line through which exhaust gas flows, the exhaust gas being generated through combustion of the fuel in the combustion device, an air preheater that is disposed in the exhaust line and that recovers heat from the exhaust gas, and a denitration device that is disposed in the exhaust line and that removes nitrogen oxide from the exhaust gas using a denitration catalyst, wherein the denitration device is disposed downstream from the air preheater in the exhaust line, and the denitration catalyst contains 43 wt% or more of vanadium pentoxide and has a BET specific surface area of 30 m^2/g or more.

[0010] In the denitration catalyst, an amount of NH_3 desorbed by NH_3-TPD (TPD: temperature programed desorption) is preferably 10.0 μmol/g or more.

[0011] The denitration device preferably removes nitrogen oxide from the exhaust gas by a selective catalytic reduction method.

[0012] The fuel is preferably natural gas.

Effects of the Invention

[0013] Since the denitration device is disposed downstream from the air preheater, the denitration catalyst used in the denitration device does not readily deteriorate. Therefore, a thermal power generation system operated at low cost can be provided.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014]

Fig. 1 illustrates a configuration of a thermal power generation system according to an embodiment of the present invention.

Fig. 2 illustrates the powder X-ray diffraction results of vanadium pentoxide catalysts produced in Example 1, Reference Examples 1 and 2, and Comparative Example 1.

Fig. 3 illustrates the powder X-ray diffraction results of vanadium pentoxide catalysts produced in Examples 1 and 2, Reference Examples 3 to 6, and Comparative Examples 2 and 3.

Fig. 4 illustrates the NH_3-SCR activity of vanadium pentoxide catalysts produced in Example 1, Reference Examples 1 and 2, and Comparative Examples 1 and 4.

Fig. 5 illustrates the relationship between the reaction temperature and the N_2 selectivity in a selective catalytic reduction reaction that uses vanadium pentoxide catalysts produced in Reference Example 1 and Comparative Example 1.

Fig. 6 illustrates the space velocity dependency in the case where a vanadium pentoxide catalyst produced in Reference Example 1 is used in an NH_3-SCR reaction.

Fig. 7 illustrates a change in the NO conversion ratio over time in the case where a vanadium pentoxide catalyst produced in Reference Example 1 is used in a selective catalytic reduction reaction in coexistence with water.

Fig. 8 illustrates changes in the NH_3, NO, and SO_2 concentrations over time in the case where a vanadium pentoxide catalyst produced in Reference Example 1 is used in a selective catalytic reduction reaction in coexistence with S.

Fig. 9 illustrates the relationship between the amount of vanadium pentoxide supported and the NO conversion ratio of a vanadium pentoxide catalyst produced in each of Examples at each reaction temperature.

Fig. 10 illustrates the relationship between the BET specific surface area and the NO conversion ratio of a vanadium pentoxide catalyst produced in each of Examples, Reference Examples, and Comparative Examples.

Fig. 11 illustrates the powder X-ray diffraction results of vanadium pentoxide catalysts produced in Examples 4 to 6 and Reference Examples 7 and 8.

Fig. 12 illustrates the NH_3-SCR activity of vanadium pentoxide catalysts produced in Examples 4 to 6 and Reference Examples 7 and 8.

Fig. 13 illustrates the relationship between the specific surface area and the NO conversion ratio of vanadium pentoxide catalysts produced in Examples 4 to 6, Reference Examples 1, 2, and 7, and Comparative Example 1.

Fig. 14 illustrates the relationship between the BET specific surface area and the amount of NH_3 desorbed of vanadium pentoxide catalysts produced in Examples 4 and 5, Reference Examples 1 and 2, and Comparative Example 1.

Fig. 15 illustrates the relationship between the amount of NH_3 desorbed and the NO conversion ratio of vanadium pentoxide catalysts produced in Examples 4 and 5, Reference Examples 1 and 2, and Comparative Example 1.

PREFERRED MODE FOR CARRYING OUT THE INVENTION

[0015] Hereafter, an embodiment of the present invention will be described with reference to the attached drawings. Fig. 1 illustrates a configuration of a thermal power generation system 1 according to this embodiment. As illustrated in Fig. 1, the thermal power generation system 1 includes a boiler 10 serving as a combustion device, a vaporizer 20, an exhaust line L1, an air preheater 30, a denitration device 40, an induced draft fan 50, and a smokestack 60.

[0016] The boiler 10 burns natural gas serving as fuel together with air. In the boiler 10, combustion of natural gas generates exhaust gas. Note that the combustion of natural gas does not generate combustion ash unlike the combustion of pulverized coal. Therefore, the thermal power generation system 1 does not necessarily include a dust collector. Furthermore, since natural gas does not contain a S component, the thermal power generation system 1 also does not necessarily include a desulfurization device.

[0017] The boiler 10 has a substantially inverted U shape on the whole. The exhaust gas generated in the boiler 10 moves along the shape of the boiler 10 so as to draw an inverted U shape. The temperature of exhaust gas near the outlet of the boiler 10 is, for example, 300°C to 400°C.

[0018] The vaporizer 20 vaporizes natural gas supplied from an LNG tank (not illustrated) and supplies the natural gas to the boiler 10. The natural gas may be vaporized by using a vaporizer that uses seawater (open rack vaporizer), a vaporizer in which natural gas is heated using hot water heated with a gas burner (submerged combustion vaporizer), or a vaporizer that performs several step heat exchanges using intermediate fluid.

[0019] The boiler 10 is connected to an upstream portion of the exhaust line L1. The exhaust line L1 is a flow pass through which the exhaust gas generated in the boiler 10 flows.

[0020] The air preheater 30 is disposed in the exhaust line L1. The air preheater 30 recovers heat from the exhaust gas by performing heat exchange between the exhaust gas and air for combustion that is sent from a forced draft fan (not illustrated). The air for combustion is heated in the air preheater 30 and then supplied to the boiler 10.

[0021] The denitration device 40 is disposed downstream from the air preheater 30 in the exhaust line L1. The exhaust gas that has been cooled in the air preheater 30 is supplied to the denitration device 40. The denitration device 40 removes nitrogen oxide from the exhaust gas using a denitration catalyst. The denitration catalyst used in the denitration device 40 will be specifically described later. The temperature of the exhaust gas in the denitration device 40 is, for example, 130°C to 200°C.

[0022] In the denitration device 40, nitrogen oxide is removed from the exhaust gas by a selective catalytic reduction method. In the selective catalytic reduction method, nitrogen and water are generated from nitrogen oxide by using a reducing agent and a denitration catalyst. Thus, nitrogen oxide can be efficiently removed from the exhaust gas. The reducing agent used in the selective catalytic reduction method contains at least one of ammonia and urea. When ammonia is used as a reducing agent, ammonia in any state, such as ammonia gas, liquid ammonia, or an aqueous ammonia solution, may be used.

[0023] More specifically, the denitration device 40 may have the following mechanism. Ammonia gas is injected to the introduced exhaust gas and then the mixed gas is brought into contact with the denitration catalyst.

[0024] The induced draft fan 50 is disposed downstream from the denitration device 40 in the exhaust line L1. In the induced draft fan 60, the exhaust gas from which nitrogen oxide has been removed in the denitration device 40 is taken in from the upstream side and sent out to the downstream side.

[0025] The smokestack 60 is connected to a downstream portion of the exhaust line L1. The exhaust gas from which nitrogen oxide has been removed in the denitration device 40 is introduced into the smokestack 60. The temperature of the exhaust gas in the denitration device 40 is, for example, 130°C to 200°C. Therefore, the exhaust gas introduced into the smokestack 60 is effectively discharged from the upper part of the smokestack 100 because of a stack effect. The temperature of the exhaust gas near the outlet of the smokestack 100 is, for example, 110°C.

[0026] Next, the denitration catalyst used in the denitration device 40 will be described. The denitration catalyst of the present invention contains 43 wt% or more of vanadium pentoxide and has a BET specific surface area of 30 m^2/g or more. Such a denitration catalyst can exhibit a high denitration effect even in a low-temperature environment compared with known denitration catalysts such as a vanadium/titanium catalyst.

[0027] Specifically, when a denitration catalyst containing 3.3 wt% or more of vanadium oxide in terms of vanadium pentoxide is used in a selective catalytic reduction reaction (NH_3-SCR) that uses ammonia as a reducing agent, the NO conversion ratio is approximately 35% or more at a reaction temperature of 120°C and approximately 60% or more at a reaction temperature of 150°C. Even at a reaction temperature of 100°C, the NO conversion ratio exceeds 20%. In contrast, if the denitration catalyst contains only less than 3.3 wt% of vanadium oxide in terms of vanadium pentoxide, the NO conversion ratio is less than 20% at a reaction temperature of 120°C and even at a reaction temperature of 150°C.

[0028] As described above, the denitration catalyst according to the present invention contains 43 wt% or more of vanadium oxide in terms of vanadium pentoxide, and may also contain titanium oxide as another component in addition to the vanadium oxide. Furthermore, a noble metal, a base metal, and a main group metal may be contained. Preferably, for example, tungsten oxide, chromium oxide, and molybdenum oxide can also be contained.

[0029] It has been described that the denitration catalyst preferably contains 43 wt% or more of vanadium oxide in terms of vanadium pentoxide. Preferably, the denitration catalyst may contain 80 wt% or more of vanadium oxide in terms of vanadium pentoxide. More preferably, the content of vanadium oxide in the denitration catalyst may be 100%.

[0030] The above-described vanadium oxide includes vanadium(II) oxide (VO), vanadium(III) trioxide (V_2O_3), vanadium(IV) dioxide (V_2O_4), and vanadium(V) pentoxide (V_2O_5), and the V element in vanadium pentoxide (V_2O_5) may have a pentavalent, tetravalent, trivalent, or divalent form in the denitration reaction.

[0031] Regarding the BET specific surface area of the denitration catalyst, for example, in the NH_3-SCR that is performed at a reaction temperature of 120°C using a denitration catalyst containing vanadium pentoxide and having a BET specific surface area of 13.5 m^2/g, the NO conversion ratio exceeds 20%. Even in the NH_3-SCR that is performed at a reaction temperature of 120°C using a denitration catalyst containing vanadium pentoxide and having a BET specific surface area of 16.6 m^2/g, the NO conversion ratio exceeds 20%. In contrast, in the NH_3-SCR that is performed at a reaction temperature of 120°C using, for example, a denitration catalyst having a BET specific surface area of 4.68 m^2/g, which is a denitration catalyst having a BET specific surface area of less than 10 m^2/g, the NO conversion ratio falls below 20%.

[0032] The BET specific surface area of the denitration catalyst is 30 m^2/g or more and may be preferably 40 m^2/g or more. More preferably, the BET specific surface area of the denitration catalyst may be 50 m^2/g or more. More preferably, the BET specific surface area of the denitration catalyst may be 60 m^2/g or more.

[0033] The BET specific surface area of the denitration catalyst is preferably measured in conformity with the conditions specified in JIS Z 8830:2013. Specifically, the BET specific surface area can be measured by a method described in

Examples below.

[0034] The denitration catalyst of the present invention is used for denitration at 200°C or lower. Preferably, the denitration catalyst is used for denitration at 160°C or higher and 200°C or lower. Thus, oxidation of SO_2 into SO_3 does not occur during the NH_3-SCR reaction.

[0035] Regarding the amount of NH_3 desorbed by NH_3-TPD (TPD: temperature programed desorption), when the amount of NH_3 desorbed exceeds 10.0 μmol/g, the NO conversion ratio of the denitration catalyst in the NH_3-SCR at a reaction temperature of 120°C is 20% or more. In contrast, when the amount of NH_3 desorbed falls below 10.0 μmol/g, the NO conversion ratio of the denitration catalyst in the NH_3-SCR at a reaction temperature of 120°C falls below 20%.

[0036] In the denitration catalyst of the present invention, the amount of NH_3 desorbed by NH_3-TPD (TPD: temperature programed desorption) is 10.0 μmol/g or more. Preferably, the amount of NH_3 desorbed by NH_3-TPD may be 20.0 μmol/g or more. More preferably, the amount of NH_3 desorbed by NH_3-TPD may be 50.0 μmol/g or more. More preferably, the amount of NH_3 desorbed by NH_3-TPD may be 70.0 μmol/g or more.

[0037] The denitration catalyst containing 3.3 wt% or more of vanadium oxide in terms of vanadium pentoxide and having a BET specific surface area of 10 m^2/g or more can be produced by any of a thermal decomposition process, a sol-gel process, and an impregnation process. Hereafter, a method for producing the denitration catalyst containing 3.3 wt% or more of vanadium pentoxide and having a specific surface area of 10 m^2/g or more by a thermal decomposition process, a sol-gel process, or an impregnation process will be described.

[0038] The thermal decomposition process includes a step of thermally decomposing a vanadate. Examples of the vanadate that may be used include ammonium vanadate, magnesium vanadate, strontium vanadate, barium vanadate, zinc vanadate, tin vanadate, and lithium vanadate.

[0039] In the thermal decomposition process, the vanadate is preferably thermally decomposed at 300°C to 400°C.

[0040] The sol-gel process includes a step of dissolving a vanadate in a chelate compound, performing drying, and performing firing. Examples of the chelate compound that may be used include compounds having a plurality of carboxy groups, such as oxalic acid and citric acid; compounds having a plurality of amino groups, such as acetylacetonate and ethylenediamine; and compounds having a plurality of hydroxy groups, such as ethylene glycol.

[0041] The sol-gel process preferably includes a step of dissolving a vanadate in a chelate compound such that the molar ratio of vanadium and the chelate compound is, for example, 1:1 to 1:5, though this is dependent on the chelate compound. Preferably, the molar ratio of the vanadate and the chelate compound may be 1:2 to 1:4.

[0042] The impregnation process includes a step of dissolving a vanadate in a chelate compound, adding a carrier, performing drying, and then performing firing. Examples of the carrier that may be used include titanium oxide, aluminum oxide, and silica. As above, examples of the chelate compound that may be used include compounds having a plurality of carboxy groups, such as oxalic acid and citric acid; compounds having a plurality of amino groups, such as acetylacetonate and ethylenediamine; and compounds having a plurality of hydroxy groups, such as ethylene glycol.

[0043] In the impregnation process, xwt% V_2O_5/TiO_2 ($x \geq 43$) may be produced as a denitration catalyst according to an embodiment of the present invention by, for example, dissolving ammonium vanadate in an oxalic acid solution, adding titanium oxide (TiO_2) serving as a carrier, performing drying, and then performing firing.

[0044] The thus-produced denitration catalyst normally contains 3.3 wt% or more of vanadium pentoxide and has a specific surface area of 10 m^2/g or more.

[0045] The combustion system 1 according to the above embodiment produces the following effects.

(1) In the combustion system 1 according to the above embodiment, the denitration device 40 is disposed downstream from the air preheater 30 in the exhaust line L1 through which the exhaust gas generated in the boiler (combustion device) 10 flows. Furthermore, in the above embodiment, the denitration catalyst containing 43 wt% or more of vanadium pentoxide and having a BET specific surface area of 30 m^2/g or more is used in the denitration device 40. Since the denitration catalyst in the above embodiment can be used for denitration at 200°C or lower, the denitration device 40 can be disposed downstream from the air preheater 30. This decreases the temperature of exhaust gas subjected to denitration with the denitration catalyst, which can suppress the deterioration of the denitration catalyst. In the combustion system 1 according to the above embodiment, a dust collector and a desulfurization device are not essential components. Therefore, the configuration of the combustion system 1 is simplified, which can reduce the installation cost.

(2) As described above, in the denitration catalyst used in the denitration device 40, the amount of NH_3 desorbed by NH_3-TPD (TPD: temperature programed desorption) is preferably 10.0 μmol/g or more. When this denitration catalyst is used in the NH_3-SCR at a reaction temperature of 120°C, the NO conversion ratio exceeds 20%.

(3) In the above embodiment, the denitration device 40 removes nitrogen oxide from the exhaust gas by a selective catalytic reduction method. In the case where nitrogen oxide is removed from the exhaust gas by a selective catalytic reduction method in the denitration device 40, if the denitration catalyst deteriorates, ammonia (or urea) used as a reducing agent leaks from the denitration device 40. As described above, the denitration device 40 is not disposed upstream from the air preheater 30 that is normally disposed near the boiler 10 in the exhaust line L1. This does

not cause clogging of the air preheater 30 due to ammonium sulfate generated as a result of reaction between ammonia and a S component in the exhaust gas. Since the clogging of the air preheater 30 is prevented in such a manner, the cost for cleaning the air preheater 30 can be reduced.

(4) In the combustion system 1 according to the above embodiment, the fuel burned in the boiler (combustion device) 10 is natural gas. When natural gas is burned in a boiler of a thermal power generation system, ammonium sulfate is not generated because the natural gas does not contain S component. Consequently, the clogging of the air preheater 30 is prevented and also there is no need to include a desulfurization device in the combustion system 1. Furthermore, since dust is not generated during combustion of natural gas, there is also no need to include a dust collector in the combustion system 1. Therefore, the configuration of the combustion system 1 is simplified, which can reduce the installation cost.

[0046] The present invention is not limited to the above embodiment, and any of modifications, improvements, and the like are included in the present invention as long as the object of the present invention is achieved.

[0047] It has been described in the above embodiment that the denitration device 40 removes nitrogen oxide from the exhaust gas by a selective catalytic reduction method. However, the present invention is not limited thereto. For example, in the present invention, the denitration device 40 may remove nitrogen oxide from the exhaust gas by a non-selective catalytic reduction method.

[0048] It has been described in the above embodiment that the denitration device 40 is disposed immediately after the air preheater 30. However, the present invention is not limited thereto. The denitration device 90 may be disposed at any position downstream from the air preheater 30. After the exhaust gas is reheated using a gas-gas heater, denitration may be performed using the denitration device 90.

[0049] In the above embodiment, the LNG thermal power generation system has been described as an example of the combustion system 1. However, the present invention is not limited thereto. For example, the present invention is applicable to an integrated gasification combined cycle.

EXAMPLES

[0050] Hereafter, Examples of the catalyst component of the present invention will be specifically described together with Reference Examples and Comparative Examples. The present invention is not limited by Examples.

1. Relationship between vanadium oxide content and specific surface area and NH_3-SCR activity

1.1 Examples and Comparative Examples

[Reference Example 1]

[0051] Ammonium vanadate (NH_4VO_3) was thermally decomposed in the air at 300°C for 4 hours to obtain vanadium pentoxide (V_2O_5). The obtained vanadium pentoxide was used as a denitration catalyst in Reference Example 1. The sample name of the denitration catalyst in Reference Example 1 was "V_2O_5_300".

[Reference Example 2]

[0052] Ammonium vanadate was thermally decomposed in the air at 400°C for 4 hours to obtain vanadium pentoxide. The obtained vanadium pentoxide was used as a denitration catalyst in Reference Example 2. The sample name of the denitration catalyst in Reference Example 2 was "V_2O_5_400".

[Comparative Example 1]

[0053] Ammonium vanadate was thermally decomposed in the air at 500°C for 4 hours to obtain vanadium pentoxide. The obtained vanadium pentoxide was used as a denitration catalyst in Comparative Example 1. The sample name of the denitration catalyst in Comparative Example 1 was "V_2O_5_500".

[Example 1]

[0054] Ammonium vanadate was dissolved in an oxalic acid solution (molar ratio of vanadium:oxalic acid = 1:3). After ammonium vanadate was completely dissolved, water in the solution was evaporated on a hot stirrer, and drying was performed in a dryer at 120°C for one night. Then, the dried powder was fired in the air at 300°C for 4 hours. The vanadium pentoxide after firing was used as a denitration catalyst in Example 1. The sample name of the denitration catalyst in Example 1 obtained by this sol-gel process was "V_2O_5_SG_300". Denitration catalysts obtained at different molar ratios of vanadium and oxalic acid when ammonium vanadate is dissolved in an oxalic acid solution will be described later.

[Comparative Example 2]

[0055] Ammonium vanadate was added to an oxalic acid solution and stirred for 10 minutes, and titanium oxide serving as a carrier was gradually added. Then, water in the solution was evaporated on a hot stirrer and drying was performed in a dryer at 120°C for one night. Subsequently, the dried powder was fired in the air at 300°C for 4 hours. As a result, the denitration catalyst after firing that contained 0.3 wt% of vanadium pentoxide was used as a denitration catalyst in Comparative Example 2. The sample name of the denitration catalyst in Comparative Example 2 was "0.3wt% V_2O_5/TiO_2".

[Comparative Example 3]

[0056] The denitration catalyst after firing that was obtained by the same method as in Comparative Example 2 and contained 0.9 wt% of vanadium pentoxide was used as a denitration catalyst in Comparative Example 3. The sample name of the denitration catalyst in Comparative Example 3 was "0.9wt% V_2O_5/TiO_2".

[Reference Example 3]

[0057] The denitration catalyst after firing that was obtained by the same method as in Comparative Example 2 and contained 3.3 wt% of vanadium pentoxide was used as a denitration catalyst in Reference Example 3. The sample name of the denitration catalyst in Reference Example 3 was "3.3wt% V_2O_5/TiO_2".

[Reference Example 4]

[0058] The denitration catalyst after firing that was obtained by the same method as in Comparative Example 2 and contained 9 wt% of vanadium pentoxide was used as a denitration catalyst in Reference Example 4. The sample name of the denitration catalyst in Reference Example 4 was "9wt% V_2O_5/TiO_2".

[Reference Example 5]

[0059] The denitration catalyst after firing that was obtained by the same method as in Comparative Example 2 and contained 20 wt% of vanadium pentoxide was used as a denitration catalyst in Reference Example 5. The sample name of the denitration catalyst in Reference Example 5 was "20wt% V_2O_5/TiO_2".

[Reference Example 6]

[0060] The denitration catalyst after firing that was obtained by the same method as in Comparative Example 2 and contained 33 wt% of vanadium pentoxide was used as a denitration catalyst in Reference Example 6. The sample name of the denitration catalyst in Reference Example 6 was "33wt% V_2O_5/TiO_2".

[Example 2]

[0061] The denitration catalyst after firing that was obtained by the same method as in Comparative Example 2 and contained 43 wt% of vanadium pentoxide was used as a denitration catalyst in Example 2. The sample name of the denitration catalyst in Example 2 was "43wt% V_2O_5/TiO_2".

[Example 3]

[0062] The denitration catalyst after firing that was obtained by the same method as in Comparative Example 2 and contained 80 wt% of vanadium pentoxide was used as a denitration catalyst in Example 3. The sample name of the denitration catalyst in Example 3 was "80wt% V_2O_5/TiO_2".

[Comparative Example 4]

[0063] An existing catalyst was used in Comparative Example 4. The existing catalyst is a catalyst in which, for example, tungsten oxide (WO_3) (content: 10.72 wt%) and silica (SiO_2)

(content: 6.25 wt%) are supported on titanium oxide (TiO_2) (content: 79.67 wt%) and which contains about 0.5% of vanadium.

1.2 Evaluation

1.2.1 Powder X-ray diffraction

(Diffraction method)

[0064] Powder X-ray diffraction analysis was performed with a Rigaku smart lab using Cu-Ka.

(Diffraction result)

[0065] Fig. 2 illustrates powder XRD patterns of Example 1 (V_2O_5_SG_300), Reference Example 1 (V_2O_5_300), Reference Example 2 (V_2O_5_400), and Comparative Example 1 (V_2O_5_500). Fig. 3 illustrates powder XRD patterns of Example 1 (V_2O_5_SG_300) and Example 2, Reference Examples 3 to 6, and Comparative Examples 2 and 3 (xwt% V_2O_5/TiO_2). In the powder XRD patterns of Example 1 (V_2O_5_SG_300), Reference Example 1 (V_2O_5_300), Reference Example 2 (V_2O_5_400), and Comparative Example 1 (V_2O_5_500), only peaks for V_2O_5 were observed regardless of the thermal decomposition temperature and the production method. In the powder XRD patterns of Example 2, Reference Examples 3 to 6, and Comparative Examples 2 and 3 (xwt% V_2O_5/TiO_2), peaks for V_2O_5 were not observed at 9 wt% or less and thus V_2O_5 is believed to be highly dispersed in TiO_2. When the amount of V_2O_5 supported was increased to 20 wt%, peaks for V_2O_5 were observed at 22.2° and 27.4°, and the V_2O_5 peak intensity increased as the amount of V_2O_5 supported was increased. On the other hand, the TiO_2 peak intensity tended to decrease.

1.2.2 Measurement of BET specific surface area

(Measurement method)

[0066] The BET specific surface area was measured with a MicrotracBEL BELSORP-max. Pretreatment was performed in an Ar atmosphere at 200°C for 2 hours, and then measurement was performed at 196°C.

(Measurement result)

[0067]

[Table 1]

BET specific surface area of vanadium pentoxide catalyst

Sample		BET specific surface area /m^2g^{-1}
Reference Example1	(V_2O_5_300)	16.6
Reference Example2	(V_2O_5_400)	13.5
Comparative Example1	(V_2O_5_500)	4.68
Example1	(V_2O_5_SG_300)	62.9
Comparative Example2	(0.3wt%V_2O_5/TiO_2)	62.8
Comparative Example3	(0.9wt%V_2O_5/TiO_2)	59
Reference Example3	(3.3wt%V_2O_5/TiO_2)	55.4
Reference Example4	(9wt%V_2O_5/TiO_2)	54.6
Reference Example5	(20wt%V_2O_5/TiO_2)	48.3
Reference Example6	(33wt%V_2O_5/TiO_2)	41.2
Example2	(43wt%V_2O_5/TiO_2)	49.4
Example3	(80wt%V_2O_5/TiO_2)	34
Comparative Example4	(Existing catalyst)	61.8

[0068] Table 1 shows BET specific surface areas of Reference Example 1 (V_2O_5_300), Reference Example 2 (V_2O_5_400), Comparative Example 1 (V_2O_5_500), Example 1 (V_2O_5_SG_300), Comparative Examples 2 and 3, Reference Examples 3 to 6, and Examples 2 and 3 (xwt% V_2O_5/TiO_2 catalyst), and Comparative Example 4 (existing catalyst). In the vanadium pentoxide catalysts obtained by thermally decomposing ammonium vanadate, the BET specific surface area decreased with increasing the thermal decomposition temperature. That is, the vanadium pentoxide in Reference Example 1 (V_2O_5_300) in which the thermal decomposition was performed at 300°C had a maximum BET specific surface area of 16.6 m^2g^{-1}. The vanadium pentoxide obtained at 300°C through a sol-gel process had a larger BET specific surface area of 62.9 m^2g^{-1}. In Reference Examples 3 to 6, Examples 2 and 3, and Comparative Examples 2 and 3 (xwt% V_2O_5/TiO_2), as the amount of vanadium pentoxide supported was increased, pores in TiO_2 were filled and the BET specific surface area decreased.

1.2.3 Measurement of catalytic activity

(Measurement method)

[0069] An NH_3-SCR reaction was performed using a fixed-bed flow reactor under the conditions listed in Table 2 below. Among gases that had passed through the catalytic layer, NO, NH_3, NO_2, and N_2O were analyzed with a Jasco FT-IR-4700.

[Table 2]

NH_3-SCR measurement conditions

Amount of catalyst	0.375mg	
Gas flow rate	250mLmin^{-1}	
	(NO: 250ppm, NH_3:	250ppm, O_2: 4vol%)
	(2000 ppm NO/Ar	31.3 mL min^{-1})
	(2000 ppm NH_3/Ar	31.3 mL min^{-1})
	(O_2	14 mL min^{-1})
	(Ar	177.4 mL min^{-1})
Space velocity	40,000 mLh^{-1}g$_{cat}^{-1}$	

[0070] Furthermore, the NO conversion ratio and the N_2 selectivity were calculated from formulae below. Herein, NO_{in} represents a NO concentration at an inlet of a reaction tube, NO_{out} represents a NO concentration at an outlet of the reaction tube, N_{2out} represents a N_2 concentration at the outlet of the reaction tube, NH_{3in} represents an NH_3 concentration at the inlet of the reaction tube, and NH_{3out} represents an NH_3 concentration at the outlet of the reaction tube.

[Formula. 1]

$$\text{NO CONVERSION RATIO} = \frac{NO_{in} - NO_{out}}{NO_{in}} \times 100$$

[Formula. 2]

$$N_2\ \text{SELECTIVITY}(\%) = \frac{2 * N_{2out}}{(NO_{in} + NH_{3in}) - (NO_{out} + NH_{3out})} \times 100$$

$$(2 * N_{2out} = (NO_{in} + NH_{3in}) - (NO_{out} + NH_{3out} + NO_{2out} + 2 * N_2O_{out}))$$

(Measurement result)

[0071] Fig. 4 illustrates the NH_3-SCR activity of the vanadium pentoxide catalysts. In the case of the catalysts obtained by thermally decomposing ammonium vanadate, the NO conversion ratio increased as the thermal decomposition temperature was decreased. The highest activity was exhibited in Reference Example 1 (V_2O_5_300°C) in which the catalyst was obtained at a thermal decomposition temperature of 300°C. At a reaction temperature of 200°C, a NO conversion ratio of 80% or more was achieved when any of the catalysts in Reference Example 1 (V_2O_5_300°C), Reference Example 2 (V_2O_5_400°C), and Example 1 (V_2O_5_SG_300°C) was used. Furthermore, the NO conversion ratio was higher in any of Examples than in Comparative Example 1 and Comparative Example 4.

[0072] The specific surface area of the vanadium pentoxide increases as the thermal decomposition temperature is decreased. Therefore, it is believed that the low-temperature NH_3-SCR activity that uses a bulk vanadium pentoxide catalyst is attributable to the BET specific surface area. Hence, as described above, the vanadium pentoxide was produced through a sol-gel process that uses oxalic acid in order to increase the BET specific surface area in Example 1. The BET specific surface area of the vanadium pentoxide produced through this process is 62.9 m^2g^{-1} as shown in Table 1, which is about four times larger than the BET specific surface areas of the vanadium pentoxides produced through a thermal decomposition process. The NO conversion ratio in Example 1 (V_2O_5_SG_300°C) was increased by 80% to 200% at 100°C to 150°C compared with the vanadium pentoxides produced through a thermal decomposition process.

[0073] The N_2 selectivity was almost 100% at any temperature. Fig. 5 illustrates, as examples, the N_2 selectivities in Reference Example 1 (V_2O_5_300°C) and Comparative Example 1 (V_2O_5_500°C).

(Space velocity dependency)

[0074] In the case where the catalyst in Reference Example 1 (V_2O_5_300°C) was used, the space velocity (for gas treatment) dependency was measured by performing the selective catalytic reduction reaction under the conditions listed in Table 3 below. Fig. 6 illustrates the measurement results. Fig. 6(a) illustrates the NO conversion ratio at a reaction temperature of 120°C. Fig. 6(b) illustrates the NO conversion ratio at a reaction temperature of 100°C. The 80% NO detoxification was about 15 $Lh^{-1}g_{cat}^{-1}$ at 120°C and about 11 $Lh^{-1}g_{cat}^{-1}$ at 100°C. In an experiment in which the space velocity was changed, the N_2 selectivity was almost 100%.

[Table 3]

NH_3-SCR measurement conditions

Reaction temperature	120 or 100°C
Amount of catalyst	0.375g, 0.750g, 1.5g
Total gas flow rate	250mLmin^{-1} (NO: 250ppm, NH_3: 250ppm, O_2: 4vol%, Ar balance)
Space velocity	10-40 $Lh^{-1}g_{cat}^{-1}$
Gas flow time	0.5h

(Reaction in coexistence with water)

[0075] An experiment of the NH_3-SCR reaction was performed using the catalyst in Reference Example 1 (V_2O_5_300°C) under the conditions listed in Table 4 below at a reaction temperature of 150°C at a space velocity of 20 $Lh^{-1}g_{cat}^{-1}$. Fig. 7 illustrates a change in the NO conversion ratio over time in the experiment. As a result of addition of 2.3% H_2O 1.5 hours after the start of the reaction, the NO conversion ratio decreased from 64% to 50%. The addition of H_2O did not change the N_2 selectivity. The N_2 selectivity was 100%. As a result of stop of the addition of water 3.5 hours after the start of the reaction, the NO conversion ratio increased to 67%.

[Table 4]

NH_3-SCR measurement conditions

Reaction temperature	150°C
Amount of catalyst	0.375g
Total gas flow rate	250mLmin^{-1} (NO: 250ppm, NH_3: 250ppm, O_2: 4vol%, Ar balance)
Space velocity	20 $Lh^{-1}g_{cat}^{-1}$

(Reaction in coexistence with S)

[0076] Under the same conditions as those of the experiment of the reaction in coexistence with water, 100 ppm SO_2 was caused to flow through a reaction gas. Fig. 8 illustrates the experimental results. No change occurred to the catalytic activity of NO. After the completion of the temperature increase to 150°C, the SO_2 concentration did not decrease though H_2O and O_2 were constantly present. Consequently, SO_2 did not react. Accordingly, the denitration catalysts in Examples were found to have S resistance.

(Relationship between amount of vanadium pentoxide supported and NO conversion ratio)

[0077] Fig. 9 illustrates the relationship between the amount of vanadium pentoxide supported and the NO conversion ratio at each reaction temperature. Fig. 9(a) illustrates the relationship between the amount of vanadium pentoxide supported and the NO conversion ratio at a reaction temperature of 120°C. Similarly, Fig. 9(b) illustrates the relationship between the amount of vanadium pentoxide supported and the NO conversion ratio at a reaction temperature of 150°C, and Fig. 9(c) illustrates the relationship at a reaction temperature of 100°C. In each of the graphs, the catalyst in which the amount of vanadium pentoxide supported is 100 wt% is the denitration catalyst V_2O_5_SG_300 produced in Example 1. The points plotted using a square indicate a NO conversion ratio of the existing catalyst in Comparative Example 4. All the graphs showed that, on the whole, the NO conversion ratio increased as the amount of vanadium pentoxide supported was increased. Herein, all the graphs showed that the catalyst in which the amount of vanadium pentoxide supported was 3.3 wt% had a higher NO conversion ratio than the catalyst in which the amount of vanadium pentoxide supported was 9.0 wt%. Specifically, as illustrated in Fig. 9(a), in the NH_3-SCR reaction at a reaction temperature of 120°C, the NO conversion ratio reached 80% when the amount of vanadium pentoxide supported was increased to 80 wt%. As illustrated in Fig. 9(b), in the NH_3-SCR reaction at a reaction temperature of 150°C, the NO conversion ratio considerably increased when the amount of vanadium pentoxide supported was increased to 3.3 wt%. As illustrated in Fig. 9(c), in the selective catalytic reduction reaction at a reaction temperature of 100°C, the denitration catalyst in which the amount of vanadium pentoxide supported was 80 wt% had a considerably increased NO conversion ratio compared with the denitration catalysts in which the amounts of vanadium pentoxide supported were 43 wt% or less.

(Relationship between BET specific surface area and NO conversion ratio)

[0078] Fig. 10(a) illustrates the relationship between the BET specific surface area and the NO conversion ratio of the denitration catalysts in which vanadium pentoxide was supported on titanium oxide. In the denitration catalyst in which vanadium pentoxide was supported on titanium oxide, as the amount of vanadium pentoxide supported was increased, the BET specific surface area decreased, but the activity increased on the whole. Fig. 10(b) illustrates the relationship between the BET specific surface area and the NO conversion ratio of both the denitration catalysts in which vanadium pentoxide was supported on titanium oxide and the denitration catalysts in which vanadium pentoxide was not supported on titanium oxide. In the catalysts in which vanadium pentoxide was not supported on titanium oxide, the activity increased with increasing the BET specific surface area.

2. V_2O_5 catalyst produced through sol-gel process

2.1 Examples (Examples 4 to 6 and Reference Examples 7 and 8)

[0079] In "Example 1" of the above-described "1.1 Examples and Comparative Examples", ammonium vanadate was dissolved in an oxalic acid solution such that the molar ratio of vanadium and oxalic acid was 1:3, then water was evaporated, drying was performed, and the resulting dried powder was fired. Thus, a denitration catalyst was produced. In the denitration catalysts of Reference Example 7, Examples 4 to 6, and Reference Example 8, the molar ratios of vanadium and oxalic acid were set to 1:1, 1:2, 1:3, 1:4, and 1:5, respectively. Specifically, as described above, ammonium vanadate was dissolved in an oxalic acid solution (molar ratio of vanadium:oxalic acid = 1:1 to 1:5). After ammonium vanadate was completely dissolved, water in the solution was evaporated on a hot stirrer, and drying was performed in a dryer at 120°C for one night. Then, the dried powder was fired in the air at 300°C for 4 hours. The sample names were given as "V_2O_5_SG_1:1" (Reference Example 7), "V_2O_5_SG_1:2" (Example 4), "V_2O_5_SG_1:3" (Example 5), "V_2O_5_SG_1:4" (Example 6), and "V_2O_5_SG_1:5" (Reference Example 8). Herein, the "V_2O_5_SG_300" in "Example 1" of "1.1 Examples and Comparative Examples" and "V_2O_5_SG_1:3" in Example 5 were substantially the same, but the sample name "V_2O_5_SG_1:3" in "Example 5" was used for the sake of convenience of description. To increase the BET specific surface area, a surfactant may be added to the oxalic acid solution. Examples of the surfactant include anionic surfactants such as hexadecyltrimethylammonium bromide (CTAB), sodium lauryl sulfate (SDS), and hexadecylamine; cationic surfactants; amphoteric surfactants; and nonionic surfactants.

2.2 Evaluation

2.2.1 Powder X-ray diffraction

(Diffraction method)

[0080] In the same manner as in 1.2.1, powder X-ray diffraction analysis was performed with a Rigaku smart lab using Cu-Ka.

(Diffraction result)

[0081] Fig. 11 illustrates powder XRD patterns of Reference Example 7, Examples 4 to 6, and Reference Example 8 (V_2O_5_SG). In the vanadium pentoxides (Reference Examples 7, 7, and 10) produced using the solutions having vanadium:oxalic acid ratios of 1:1, 1:2, and 1:5, only peaks for orthorhombic V_2O_5 were detected. In the vanadium pentoxides (Examples 5 and 6) produced using the solutions having vanadium:oxalic acid ratios of 1:3 and 1:4, an unidentified peak was detected at 11° in addition to the peaks for orthorhombic V_2O_5. However, the peak has not been identified yet.

2.2.2 Measurement of BET specific surface area

(Measurement method)

[0082] In the same manner as in 1.2.3, the BET specific surface area was measured with a MicrotracBEL BELSORP-max. Pretreatment was performed in an Ar atmosphere at 200°C for 2 hours, and then measurement was performed at 196°C.

(Measurement result)

[0083]

[Table 5]

BET specific surface area of vanadium pentoxide catalyst

Catalyst		BET specific surface area before reaction /m^2g^{-1}	BET specific surface area after reaction /m^2g^{-1}
Reference Example7	(V_2O_5_SG_1:1)	29.9	n.d.
Example4	(V_2O_5_SG_1:2)	33.5	n.d.
Example5	(V_2O_5_SG_1:3)	62.9	43.4
Example6	(V_2O_5_SG_1:4)	57.0	n.d.
Reference Example8	(V_2O_5_SG_1:5)	n.d.	n.d.

[0084] Table 5 shows BET specific surface areas of Reference Example 7 (V_2O_5_SG_1:1), Example 4 (V_2O_5_SG_1:2), Example 5 (V_2O_5_SG_1:3), Example 6 (V_2O_5_SG_1:4), and Reference Example 8 (V_2O_5_SG_1:5). As the ratio of the oxalic acid was increased, the specific surface area increased at vanadium:oxalic acid ratios of 1:1 to 1:3. When the ratio of the oxalic acid was further increased, the specific surface area decreased. The specific surface area in Example 5 (V_2O_5_SG_1:3) after the catalytic activity test described below considerably decreased to 43.4 m^2g^{-1} compared with the specific surface area before the catalytic activity test.

2.2.3 Measurement of catalytic activity

(Measurement method)

[0085] By the same measurement method as in 1.2.4, the NH_3-SCR activity of each V_2O_5_SG catalyst was measured and the NO conversion ratio was calculated.

(Measurement result)

[0086] Fig. 12 illustrates the NH_3-SCR activity of each V_2O_5_SG catalyst. Fig. 12(a) illustrates the NO conversion ratio plotted against reaction temperature in the NH_3-SCR reaction that uses each catalyst. Fig. 12(b) illustrates the relationship between the vanadium:oxalic acid ratio and the NO conversion ratio at a reaction temperature of 120°C. In the catalyst of Example 5 (V_2O_5_SG_1:3) having a vanadium:oxalic acid ratio of 1:3, the highest NO conversion ratio was achieved. When the oxalic acid was further added, the NO conversion ratio decreased. The NO conversion ratio in Example 6 (V_2O_5_SG_1:4) was lower than that in Example 4 (V_2O_5_SG_1:2) despite the fact that the specific surface area in Example 6 was larger than that in Example 4.

(Relationship between specific surface area and NO conversion ratio)

[0087] Fig. 13 illustrates the relationship between the BET specific surface area and the NO conversion ratio in Examples 4 to 6 and Reference Example 7 (V_2O_5_SG), Reference Example 1 (V_2O_5_300), Reference Example 2 (V_2O_5_400), and Comparative Example 1 (V_2O_5_500). The point plotted using a square indicates the relationship between the BET specific surface area and the NO conversion ratio after the selective catalytic reduction reaction in Example 5 (V_2O_5_SG_1:3). As described above, it was shown that the highest NO conversion ratio was achieved in the catalyst of Example 5 (V_2O_5_SG_1:3) having a vanadium:oxalic acid ratio of 1:3.

2.2.4 Characterization by NH_3-TPD

(Measurement method)

[0088] The amount of acid sites on the surface of the catalyst can be estimated by NH_3-TPD (TPD: temperature programed desorption). In a BELCAT manufactured by MicrotracBEL Corp., 0.1 g of each of the catalysts in Reference Example 1 (V_2O_5_300), Reference Example 2 (V_2O_5_400), Comparative Example 1 (V_2O_5_500), Example 4 (V_2O_5_SG_1:2), and Example 5 (V_2O_5_SG_1:3) was pretreated at 300°C for 1 hour while He (50 ml/min) was caused to flow. Then, the temperature was decreased to 100°C, and 5% ammonia/He (50 ml/min) was caused to flow for 30 minutes to adsorb ammonia. The flow gas was changed to He (50 ml/min) and this state was kept for 30 minutes for stabilization. Then, the temperature was increased at 10 °C/min and ammonia, which has a mass number of 16, was monitored with a mass spectrometer.

(Measurement result)

[0089]

[Table 6]
Measured amount of NH_3 desorbed by NH_3-TPD

Catalyst		Amount of NH_3 desorbed/ $\mu molg^{-1}$
Reference Example1	(V_2O_5_300)	22.9
Reference Example2	(V_2O_5_400)	14.0
Comparative Example1	(V_2O_5_500)	5.21
Example4	(V_2O_5_SG_1:2)	51.4
Example5	(V_2O_5_SG_1:3)	77.5

[0090] Table 6 shows the measurement results of the amount of NH_3 desorbed when the catalysts in Reference Example 1 (V_2O_5_300), Reference Example 2 (V_2O_5_400), Comparative Example 1 (V_2O_5_500), Example 4 (V_2O_5_SG_1:2), and Example 5 (V_2O_5_SG_1:3) were used.

[0091] Fig. 14 is a graph obtained by plotting the amount of NH_3 desorbed as a function of the BET specific surface area of each catalyst. The graph in Fig. 14 showed that the amount of NH_3 desorbed increased substantially in proportion to the BET specific surface area of V_2O_5. Fig. 15 is a graph obtained by plotting the NO conversion ratio as a function of the amount of NH_3 desorbed in each catalyst. The graph showed that the NO conversion ratio increased as the catalyst had a larger amount of NH_3 desorbed, that is, a larger amount of acid sites on the surface of the catalyst.

[0092] As described above, the denitration catalyst of the present invention that contains 3.3 wt% or more of vanadium oxide in terms of vanadium pentoxide and has a specific surface area of 10 m^2/g or more exhibits a high denitration efficiency at a low temperature of 200°C or lower in the selective catalytic reduction reaction that uses ammonia as a reducing agent. On the other hand, oxidation of SO_2 is not found.

EXPLANATION OF REFERENCE NUMERALS

[0093]

1	combustion system
10	boiler
30	air preheater
40	denitration device
L1	exhaust line

Claims

1. A combustion system comprising:

a combustion device that burns fuel;
an exhaust line through which exhaust gas flows, the exhaust gas being generated through combustion of the fuel in the combustion device;
an air preheater that is disposed in the exhaust line and that recovers heat from the exhaust gas; and
a denitration device that is disposed in the exhaust line and that removes nitrogen oxide from the exhaust gas using a denitration catalyst,
wherein the denitration device is disposed downstream from the air preheater in the exhaust line, and
the denitration catalyst contains 43 wt% or more of vanadium pentoxide and has a BET specific surface area of 30 m^2/g or more.

2. The combustion system according to Claim 1, wherein in the denitration catalyst, an amount of NH_3 desorbed by NH_3-TPD (TPD: temperature programed desorption) is 10.0 μmol/g or more.

3. The combustion system according to Claim 1 or 2, wherein the denitration device removes nitrogen oxide from the exhaust gas by a selective catalytic reduction method.

4. The combustion system according to any one of Claims 1 to 3, wherein the fuel is natural gas.

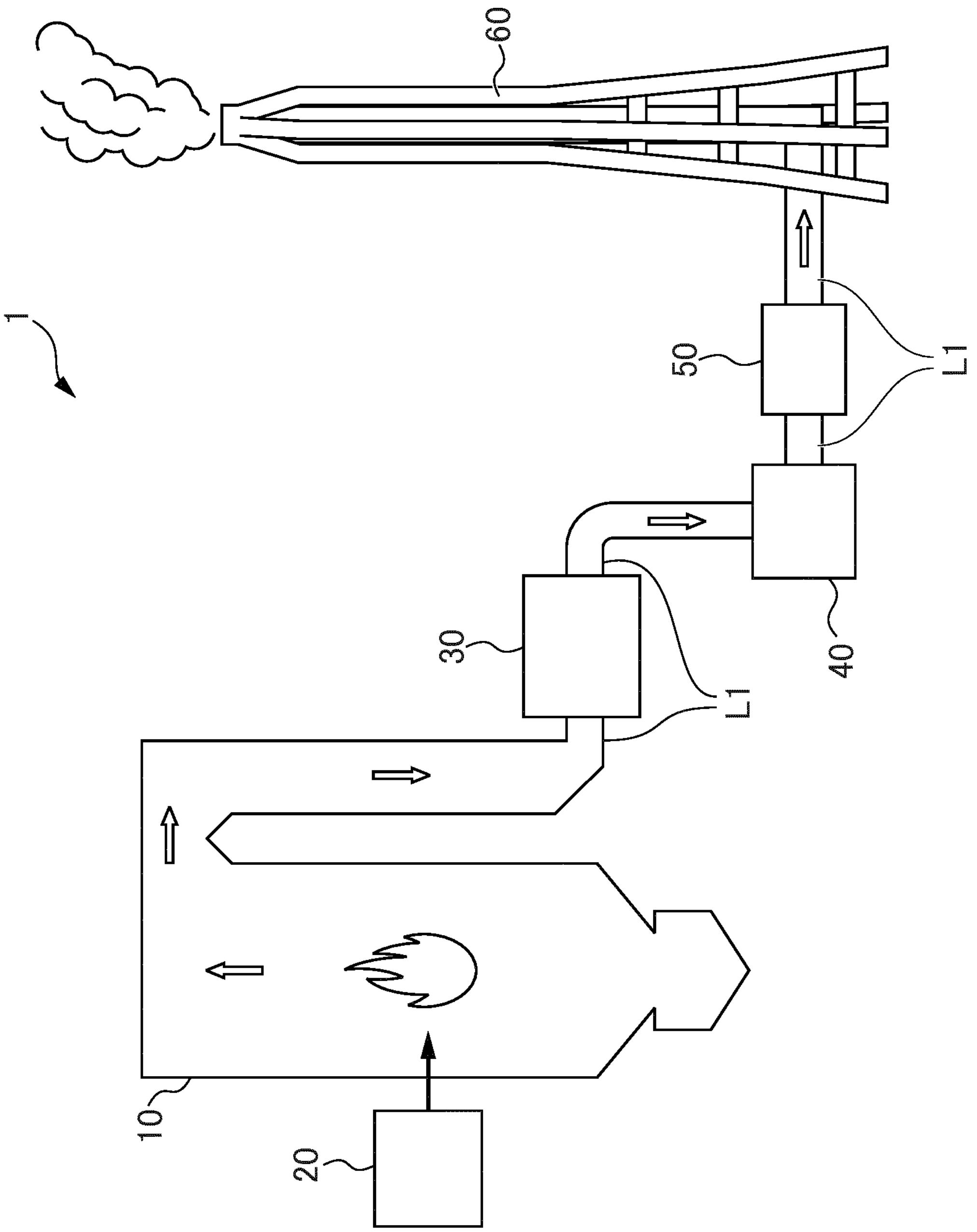


FIG. 1

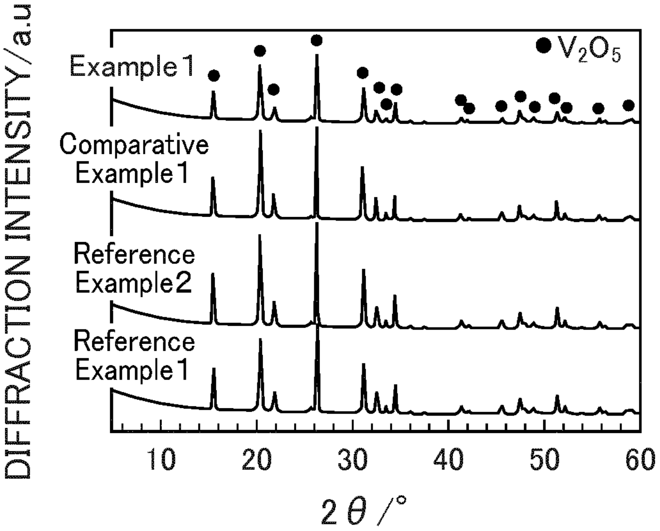

DIFFRACTION INTENSITY/a.u
● V_2O_5
Example1
Comparative Example1
Reference Example2
Reference Example1
10
20
30
40
50
60
2θ/°

FIG. 2

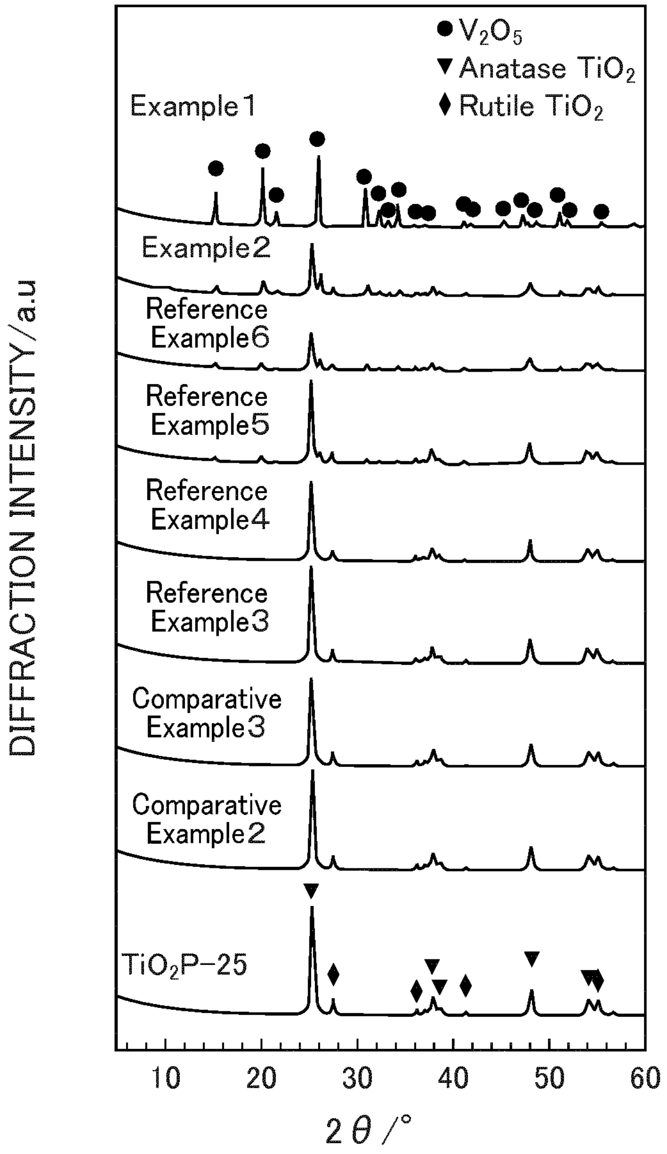

● V_2O_5
▼ Anatase TiO_2
♦ Rutile TiO_2
Example1
Example2
Reference Example6
Reference Example5
Reference Example4
Reference Example3
Comparative Example3
Comparative Example2
TiO_2P-25
DIFFRACTION INTENSITY/a.u
10
20
30
40
50
60
$2\theta/°$

FIG. 3

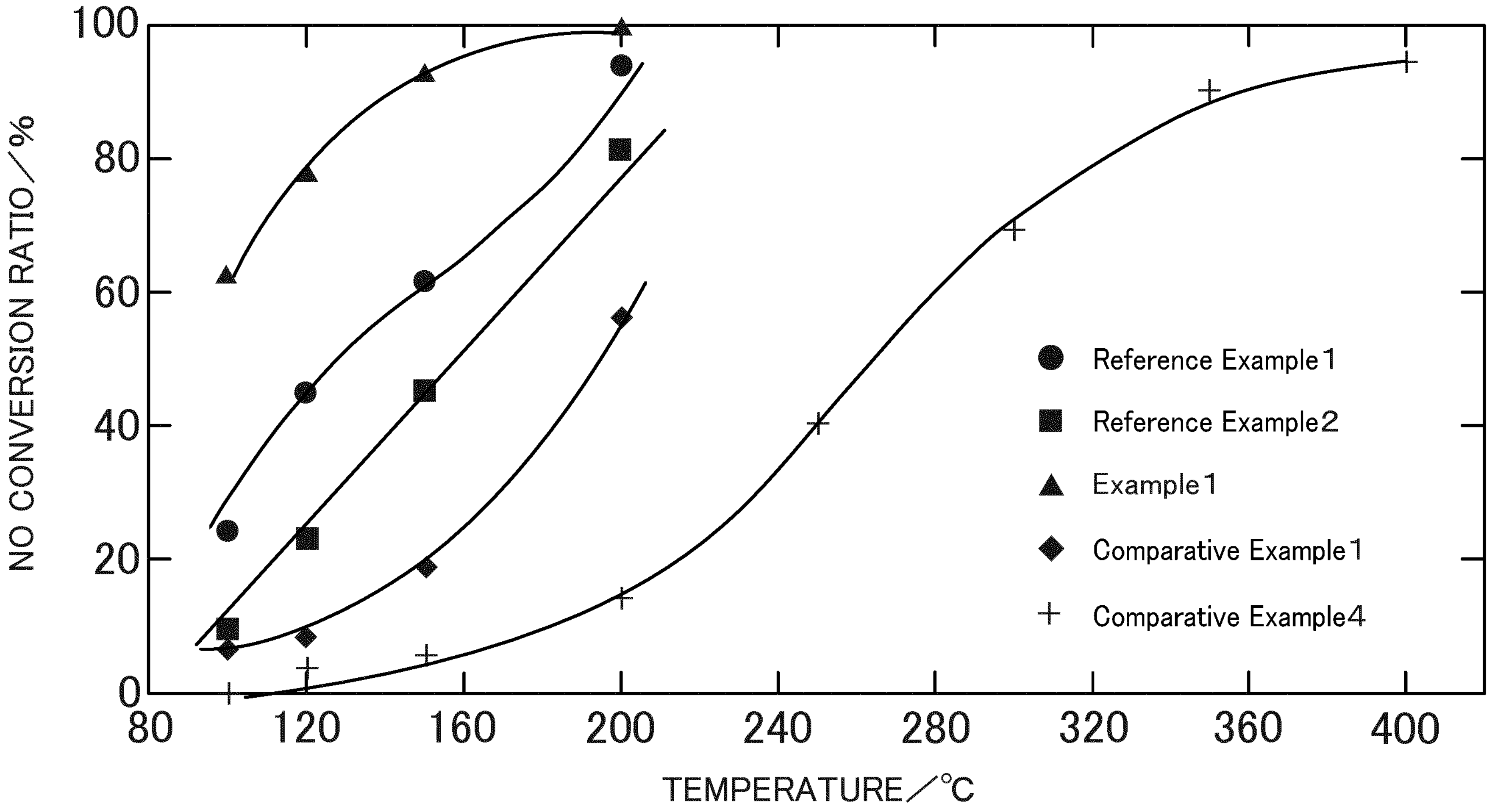

100
80
60
40
20
0
NO CONVERSION RATIO／%
80
120
160
200
240
280
320
360
400
TEMPERATURE／°C
● Reference Example1
■ Reference Example2
▲ Example1
◆ Comparative Example1
+ Comparative Example4

FIG. 4

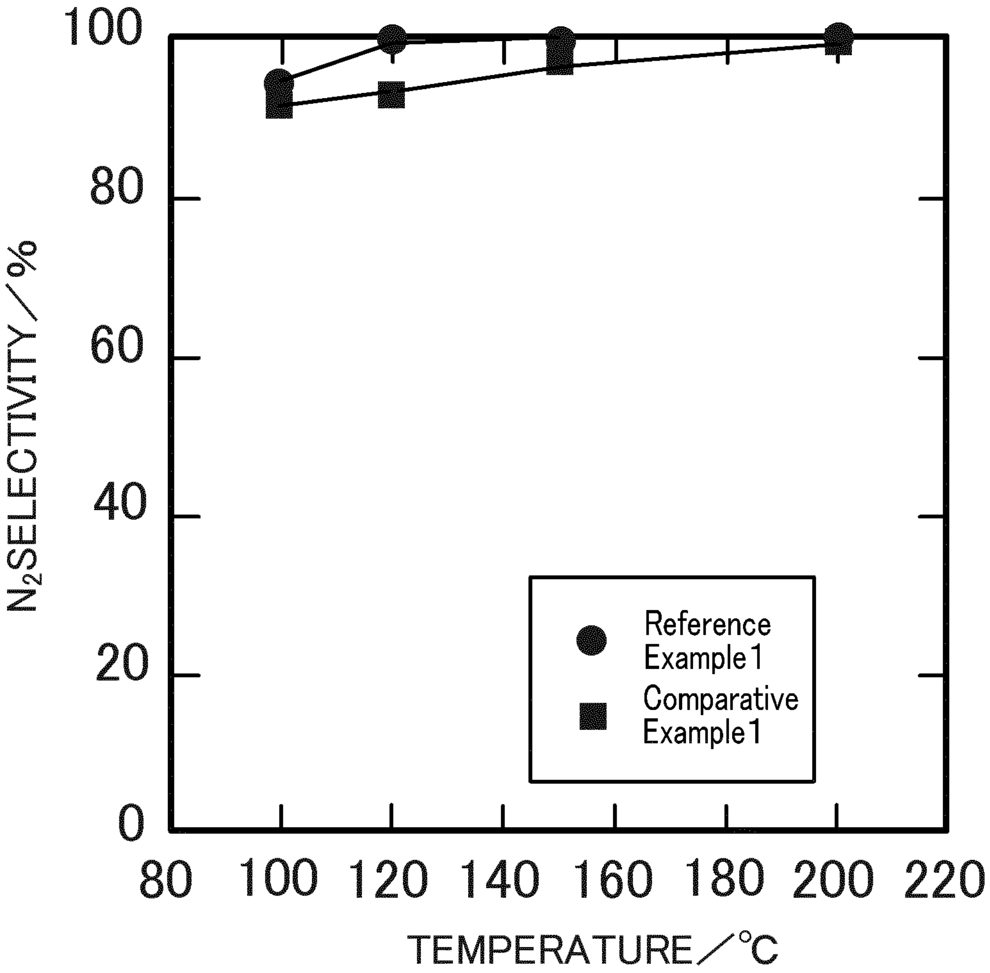

100
80
60
40
20
0
N2SELECTIVITY／%
80
100
120
140
160
180
200
220
TEMPERATURE／°C
Reference Example1
Comparative Example1

FIG. 5

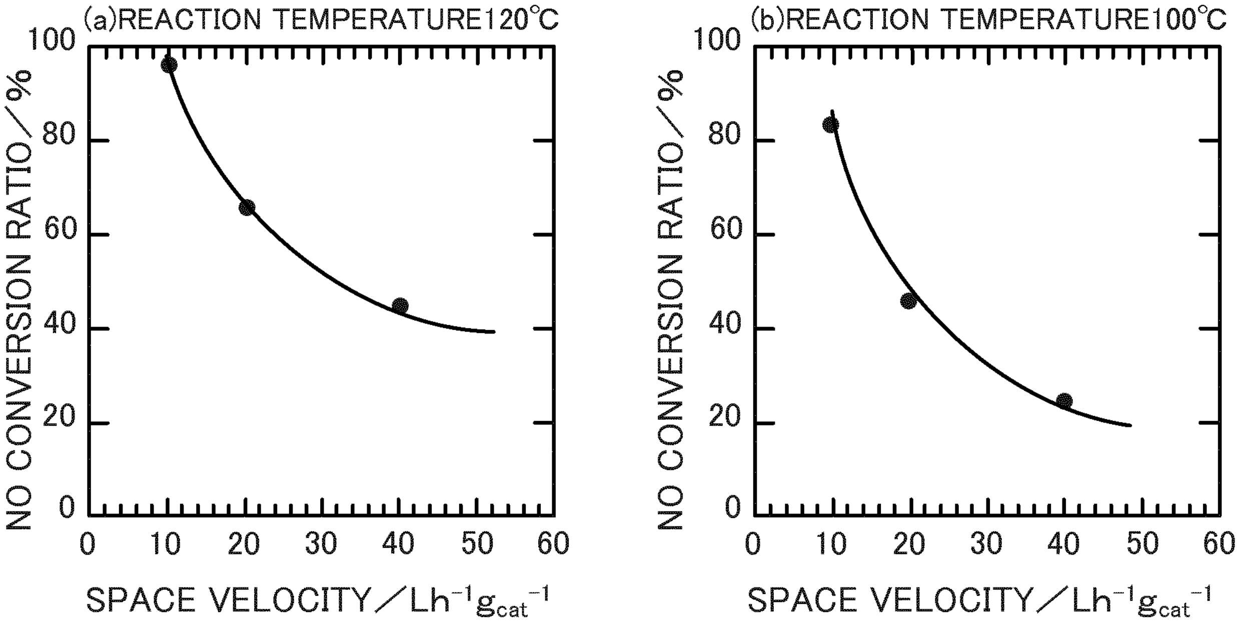

(a)REACTION TEMPERATURE120℃
(b)REACTION TEMPERATURE100℃
NO CONVERSION RATIO／%
100
80
60
40
20
0
0
10
20
30
40
50
60
SPACE VELOCITY／Lh^{-1}g$_{cat}^{-1}$

FIG. 6

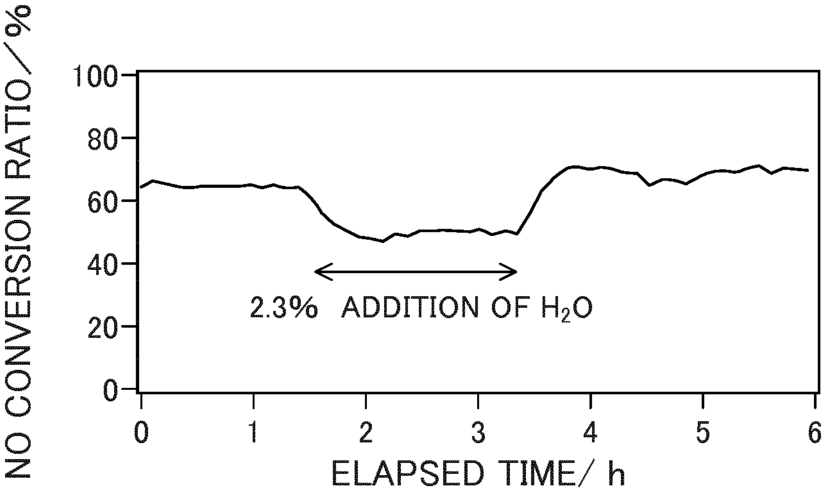

NO CONVERSION RATIO／%
100
80
60
40
20
0
0
1
2
3
4
5
6
ELAPSED TIME/ h
2.3% ADDITION OF H_2O

FIG. 7

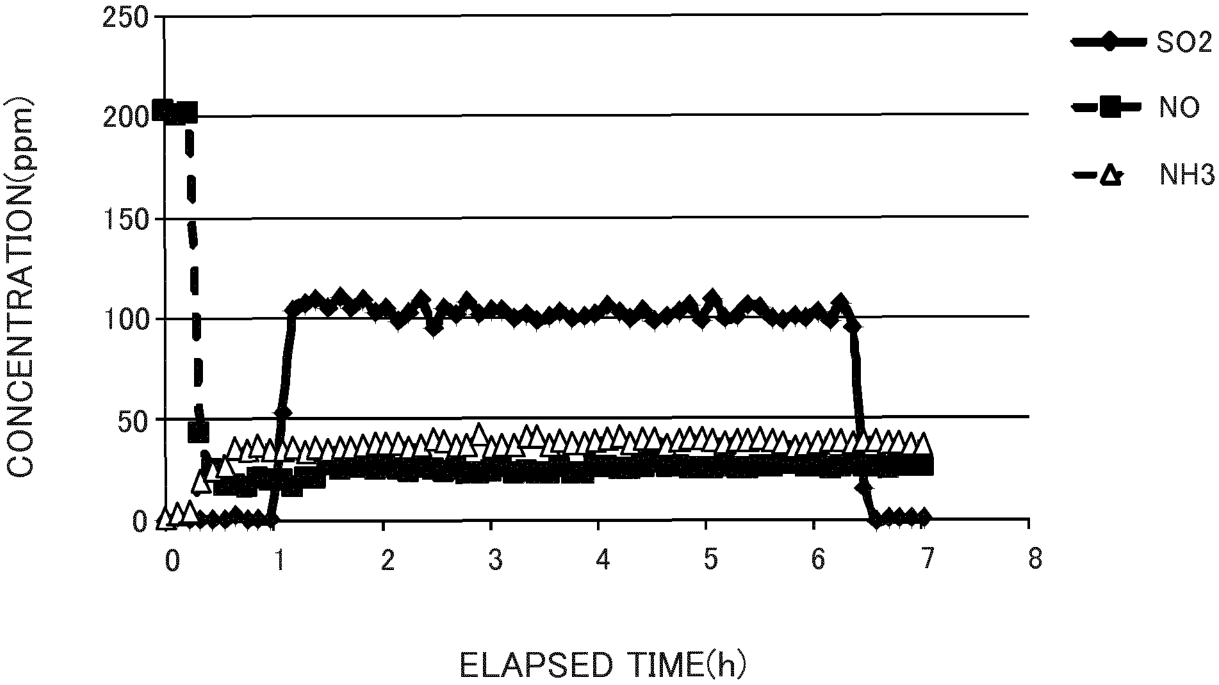

CONCENTRATION(ppm)
250
200
150
100
50
0
0
1
2
3
4
5
6
7
8
ELAPSED TIME(h)
SO2
NO
NH3

FIG. 8

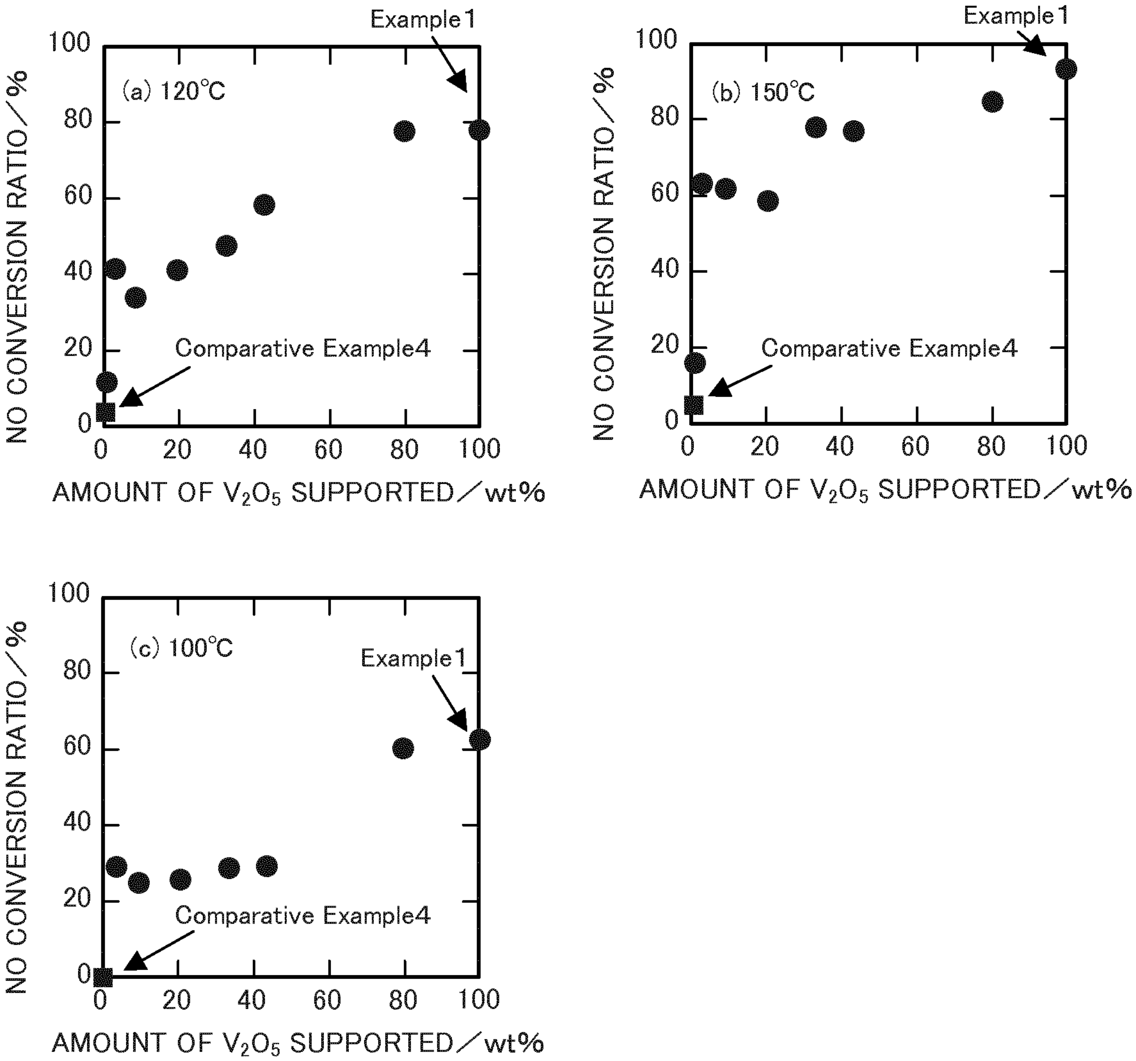
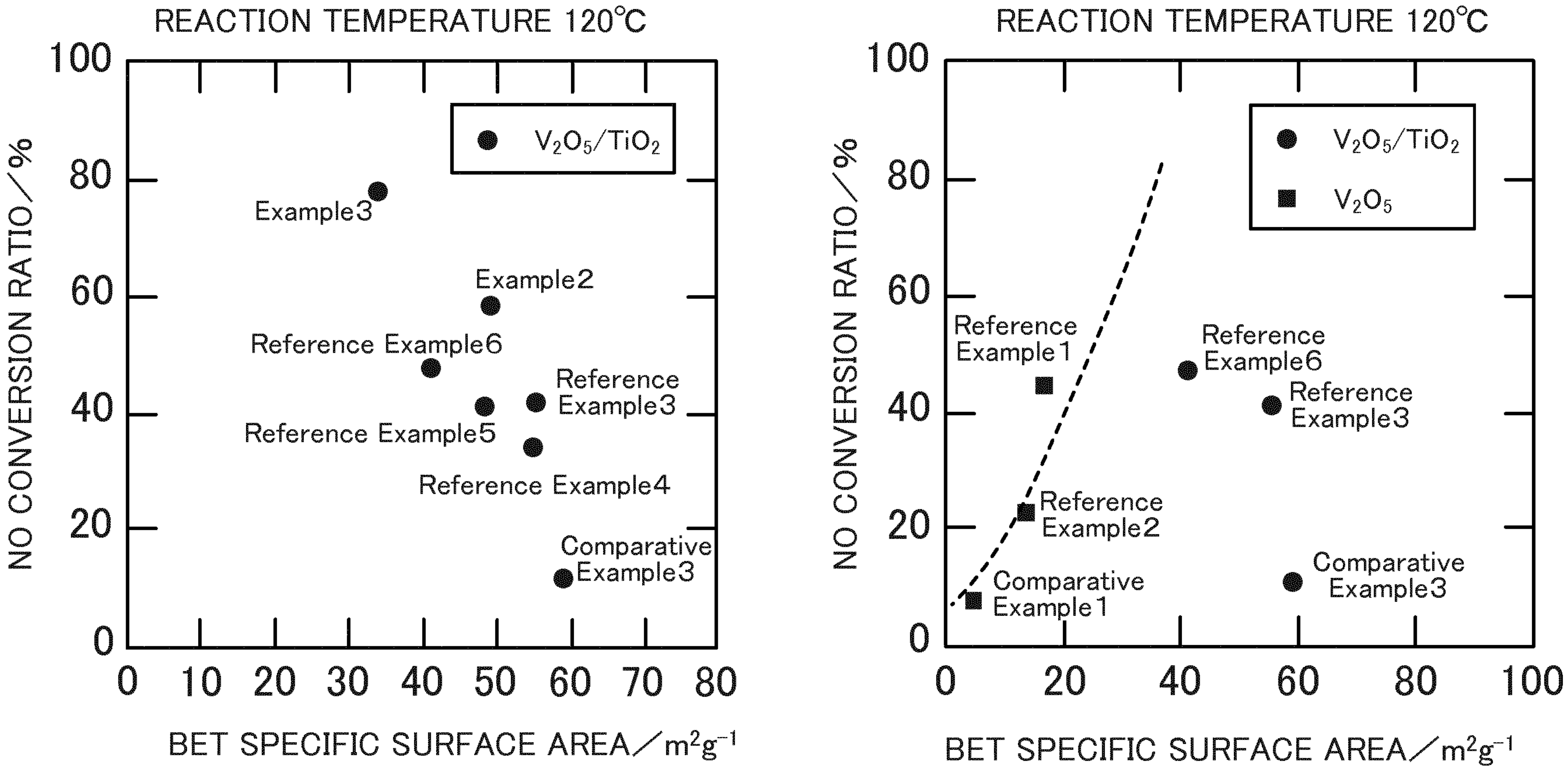

Example1
(a) 120℃
Comparative Example4
NO CONVERSION RATIO／%
AMOUNT OF V_2O_5 SUPPORTED／wt%
0
20
40
60
80
100
(b) 150℃
Example1
Comparative Example4
NO CONVERSION RATIO／%
AMOUNT OF V_2O_5 SUPPORTED／wt%
(c) 100℃
Example1
Comparative Example4
NO CONVERSION RATIO／%
AMOUNT OF V_2O_5 SUPPORTED／wt%

FIG. 9


REACTION TEMPERATURE 120°C
NO CONVERSION RATIO／%
BET SPECIFIC SURFACE AREA／m^2g^{-1}
0
20
40
60
80
100
0
10
20
30
40
50
60
70
80
● V_2O_5/TiO_2
Example3
Example2
Reference Example6
Reference Example3
Reference Example5
Reference Example4
Comparative Example3
REACTION TEMPERATURE 120°C
NO CONVERSION RATIO／%
BET SPECIFIC SURFACE AREA／m^2g^{-1}
0
20
40
60
80
100
0
20
40
60
80
100
● V_2O_5/TiO_2
■ V_2O_5
Reference Example1
Reference Example6
Reference Example3
Reference Example2
Comparative Example1
Comparative Example3

(a) (b)

FIG. 10

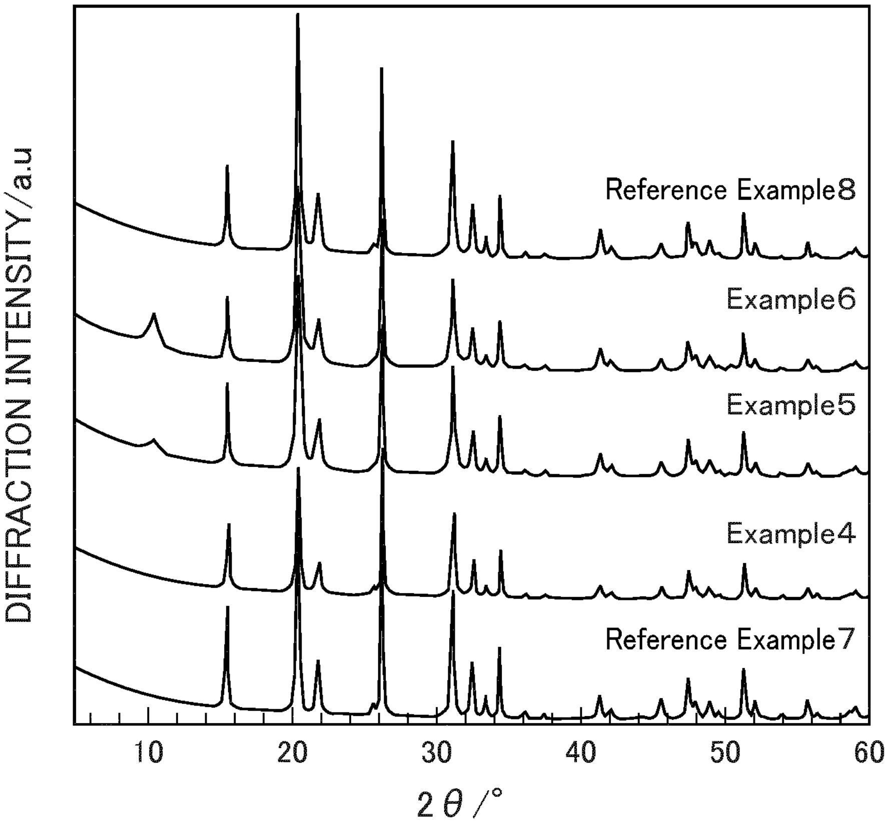
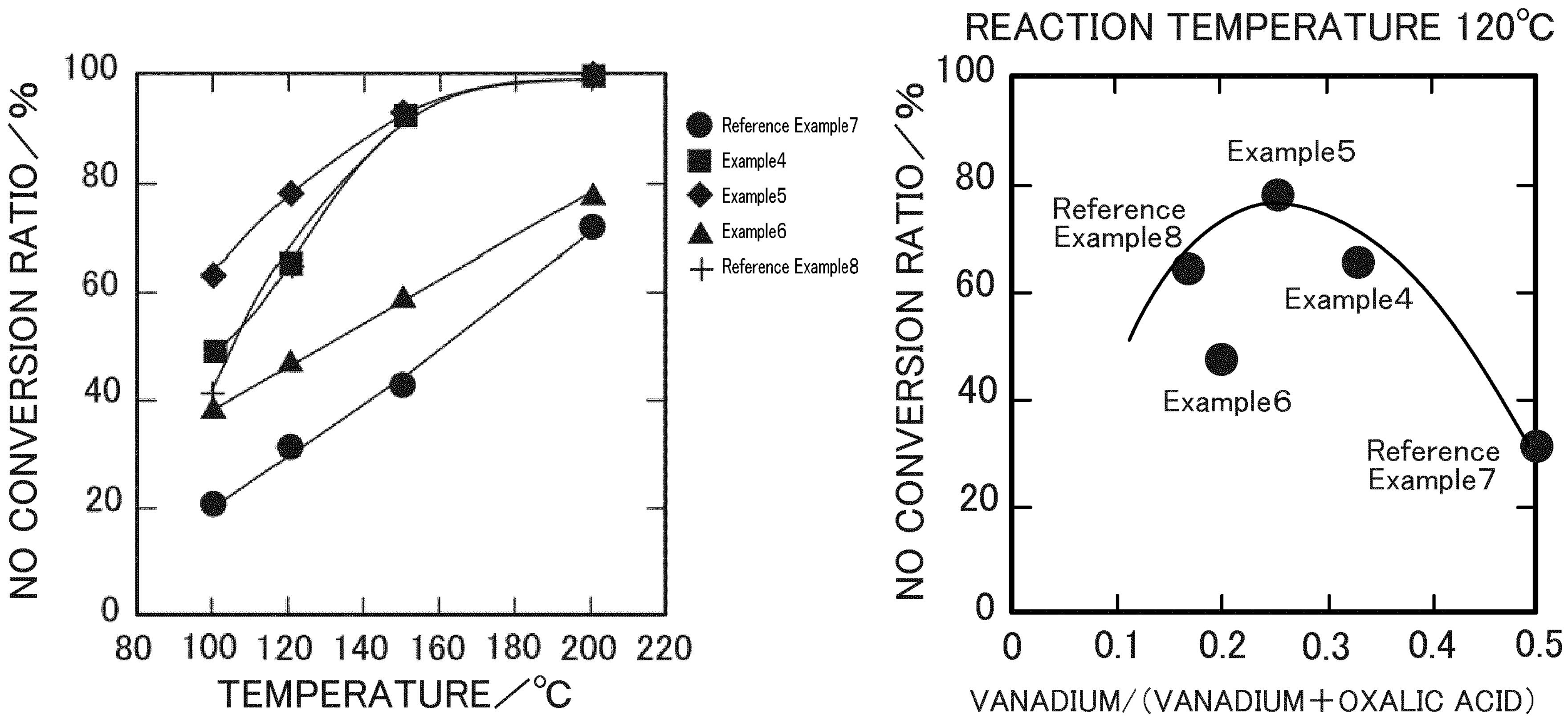

DIFFRACTION INTENSITY/a.u
Reference Example8
Example6
Example5
Example4
Reference Example7
10
20
30
40
50
60
2θ/°

FIG. 11


NO CONVERSION RATIO／%
100
80
60
40
20
0
80
100
120
140
160
180
200
220
TEMPERATURE／°C
● Reference Example7
■ Example4
◆ Example5
▲ Example6
+ Reference Example8
REACTION TEMPERATURE 120°C
NO CONVERSION RATIO／%
100
80
60
40
20
0
0
0.1
0.2
0.3
0.4
0.5
VANADIUM/（VANADIUM＋OXALIC ACID）
Example5
Reference Example8
Example4
Example6
Reference Example7

(a)

(b)

FIG. 12

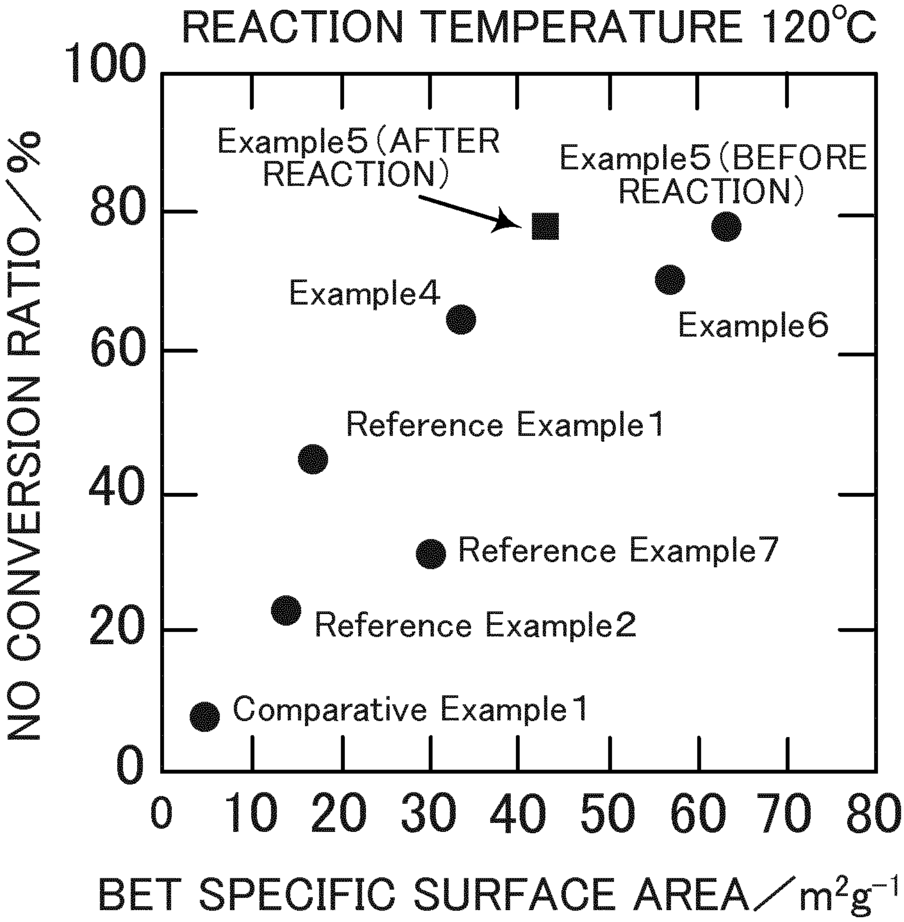

REACTION TEMPERATURE 120°C
NO CONVERSION RATIO／%
100
80
60
40
20
0
0
10
20
30
40
50
60
70
80
BET SPECIFIC SURFACE AREA／m²g⁻¹
Example5 (AFTER REACTION)
Example5 (BEFORE REACTION)
Example4
Example6
Reference Example1
Reference Example7
Reference Example2
Comparative Example1

FIG. 13

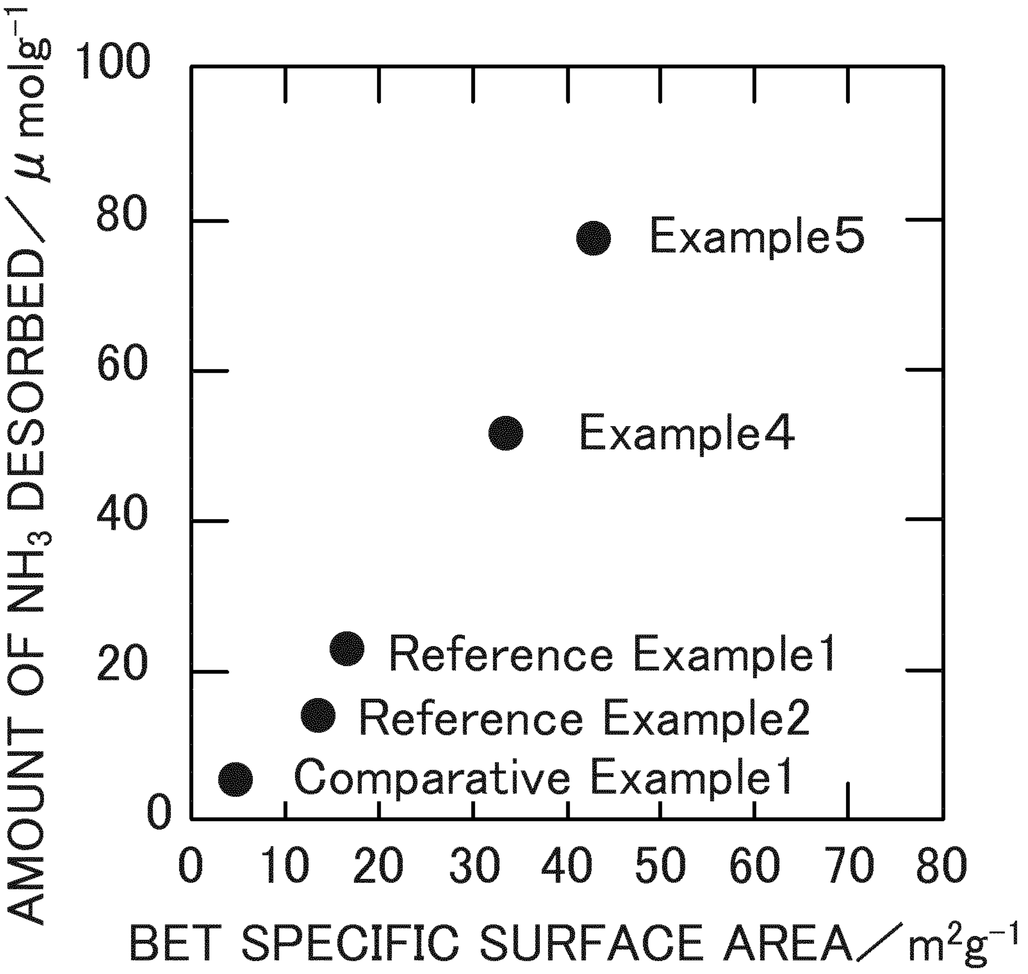

AMOUNT OF NH3 DESORBED／μmolg-1
100
80
60
40
20
0
0
10
20
30
40
50
60
70
80
BET SPECIFIC SURFACE AREA／m2g-1
Example5
Example4
Reference Example1
Reference Example2
Comparative Example1

FIG. 14

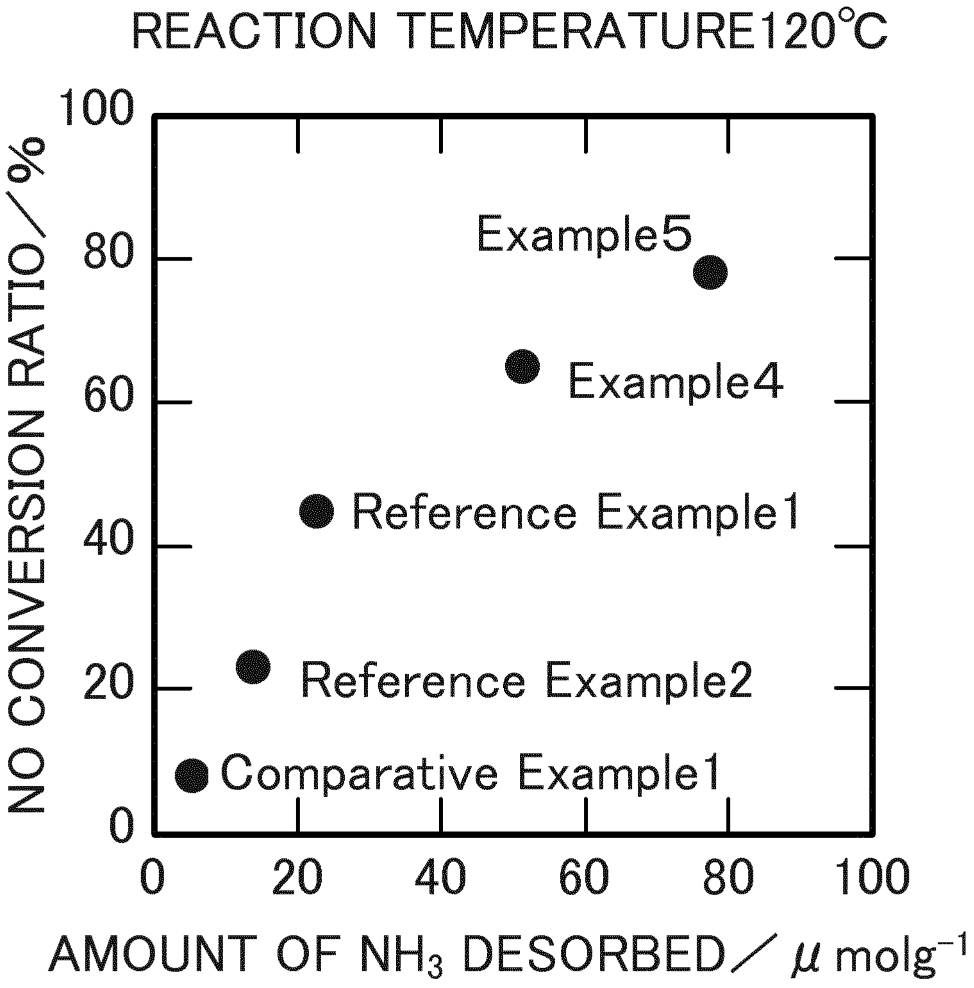

REACTION TEMPERATURE120℃
NO CONVERSION RATIO／%
100
80
60
40
20
0
0
20
40
60
80
100
Example5
Example4
Reference Example1
Reference Example2
Comparative Example1
AMOUNT OF NH_3 DESORBED／μ molg^{-1}

FIG. 15

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2017/009049

A. CLASSIFICATION OF SUBJECT MATTER
F23J15/00(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
F23J15/00, B01D53/86, B01D53/90, B01J23/22

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2017
Kokai Jitsuyo Shinan Koho	1971-2017	Toroku Jitsuyo Shinan Koho	1994-2017

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2005-342710 A (Mitsubishi Chemical Engineering Corp.), 15 December 2005 (15.12.2005), entire text; all drawings (Family: none)	1-4
A	JP 54-66390 A (Yasushi KUBO, Masaharu KANEKO), 28 May 1979 (28.05.1979), entire text; all drawings (Family: none)	1-4
A	JP 6-277512 A (Mitsui Mining Co., Ltd.), 04 October 1994 (04.10.1994), entire text; all drawings & US 5696049 A & WO 1994/021373 A1 & EP 643991 A1	1-4

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
“A” document defining the general state of the art which is not considered to be of particular relevance
“E” earlier application or patent but published on or after the international filing date
“L” document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
“O” document referring to an oral disclosure, use, exhibition or other means
“P” document published prior to the international filing date but later than the priority date claimed
“T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
“X” document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
“Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
“&” document member of the same patent family

Date of the actual completion of the international search
21 April 2017 (21.04.17)

Date of mailing of the international search report
09 May 2017 (09.05.17)

Name and mailing address of the ISA/
Japan Patent Office
3-4-3,Kasumigaseki,Chiyoda-ku,
Tokyo 100-8915,Japan

Authorized officer

Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2017/009049

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2015-533766 A (Nanjing Tech University), 26 November 2015 (26.11.2015), entire text; all drawings & US 2015/0246823 A1 & WO 2014/047937 A1	1-4
A	JP 59-217414 A (Babcock-Hitachi Kabushiki Kaisha), 07 December 1984 (07.12.1984), entire text; all drawings (Family: none)	1-4
A	JP 11-253754 A (Mitsubishi Chemical Corp.), 21 September 1999 (21.09.1999), entire text; all drawings (Family: none)	1-4
A	JP 2011-190940 A (Hitachi, Ltd.), 29 September 2011 (29.09.2011), entire text; all drawings (Family: none)	1-4
E,A	JP 6093101 B1 (The Chugoku Electric Power Co., Inc.), 08 March 2017 (08.03.2017), entire text; all drawings (Family: none)	1-4
E,A	WO 2017/042895 A1 (The Chugoku Electric Power Co., Inc.), 16 March 2017 (16.03.2017), entire text; all drawings (Family: none)	1-4

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REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- JP 2011190940 A **[0005]**